Coal-Tar Pitch Utilization

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ABSTRACT
Coal tar pitch has been traditionally used in the aluminium and graphite industry as a binder for anode and electrode manufacture. Further, coal-tar pitches have been studied as matrix precursors in carbon-carbon composites for carbon foam preparation and for energy storage carbons among others. The possibility of obtaining a wide range of carbon materials of different structure and properties, depending on the characteristics of the parent pitch, or even from the same pitch by simply changing the experimental conditions, makes pitch a very suitable product for the tailoring of carbon materials. The problem with coal-tar pitch is the presence of inherent primary QI which impedes it direct use in such applications, such as carbon fibres. A preliminary filtration step is required to remove the QI particles. Currently, improved coal-based pitches are in the process of being developed from tar fractions, such as anthracene-oil with no QI, with the aim of obtaining graphitic materials. This paper offers an overview of traditional uses of coal tar pitches, their main markets and their potential as carbon material precursors.

Keywords
Coal-tar pitch, carbon materials, anodes

COAL-TAR PITCH HISTORY

Coal-tar pitches (CTP) are coal conversion products, which have been used since long time ago. However, their application as a profitable industrial material start at the end of the XIX and beginning of the XX centuries, when CTP started to be used in different areas related to the technologies of carbon production (e.g., carbon anodes). The event that led to the mass irruption of CTPs onto the market was probably the substitution of the traditional and obsolete beehive coke ovens by coke-making facilities, such those developed by Koppers at the beginning of the XX century. These facilities produced coke of good quality, while at the same time all the by-products generated during the coking process (e.g., coal tar) could be recovered and subsequently transformed. This event could be considered as the industrial birth of coal-tar pitch.

Because of their affinity and binding capacities to other carbon products (e.g., petroleum coke), CTPs promptly found application in the fabrication of carbon artefacts for the aluminium industry. The Hall-Héroult process, developed at the end of the XIX century, required a large amount of binder for making carbon anodes. This gave a great impulse to the production of CTP with CTP production constantly increasing during the XX century to reach production levels of ~ 8 Mt/year. Nowadays, CTPs are not only an irreplaceable binder in the aluminium industry but also have widened their fields of application to other industrial sectors, such as graphite electrodes for electric arc furnaces, refractory briquettes, etc.

However, the restrictive legislation concerning the emissions of pollutants to the atmosphere and the sharp decline in coal tar supply as a consequence of the closing down of numerous coke ovens have made it necessary to find an alternative binder that is more environmentally-friendly and that can fill the
gap left by the progressive coal tar deficit. Some of the strategies pursued to address these problems are for example the development of hybrid pitches based on blends of CTP and petroleum pitch in different ratios or the development of pitches based on coal tar fractions, i.e., anthracene oil-based pitches. Both solutions seem to be encouraging from the point of view of alternative more environmentally-friendly feedstocks. Anthracene oil is a promising raw material that could be used for the production of pitches and a semi-industrial plant is operating already in Oviedo (Spain) with a capacity of anthracene oil processing of 7t/year.

It is evident that the production of CTPs is dependently on their industrial consumption in the applications described above. However, it must be borne in mind that CTP is an excellent source of polycyclic aromatic compounds (PACs) that can be easily polymerized/condensed giving rise to graphitic materials. For this reason, CTPs have also found application in other specialty fields where highly structural, mechanical, electrical and thermal properties are required. Carbon fibres, polygranular graphites, needle coke, carbon-carbon composites are some of the areas in which CTPs are used, especially for scientific purposes.

PREPARATION AND MODIFICATION OF PITCHES FROM COAL-TAR AND THEIR FRACTIONS

The industrial production of CTPs consists of the fractionated distillation of the coal tar at temperatures near to 400 °C (Figure 1). By this procedure, the coal tar yields a series of liquid fractions suitable for different industrial applications and a residue which is solid at room temperature, called coal tar pitch. Two different types of CTPs are usually produced: binder and impregnating-grade. The main difference between these pitches resides in the quinoline insoluble content (much lower in the impregnating CTPs) and in the softening point (~110 °C, for binder and ~90 °C, for impregnating grade). The heaviest coal tar distillation fraction, which distils between ~270-400 °C, is anthracene oil.
This fraction, composed of 3-5 ring aromatic ring PACs, has eluded all attempts at polymerization by conventional thermal treatments at atmospheric pressure. Its transformation into a pitch requires the use of specialized forms of treatment that allow the polymerization of low-molecular weight PACs to take place. Industrial Química del Nalón, S.A. in collaboration with INCAR-CSIC has developed an industrial procedure to transform anthracene oil into pitches. This procedure involves thermal oxidative condensation and subsequent thermal treatment and distillation until the pitch reaches the desired softening point (Figure 1).

This type of pitches is produced with the specific aim of fulfilling the requirements for binder and impregnations agents, mainly for carbon anodes and graphite electrodes. For this reason, their use in other fields, such as precursors for advanced carbon materials, usually requires a pre-treatment of the commercial pitches in order to adapt their composition and characteristics for their further utilization. For example, thermal treatment in an inert atmosphere and air-blowing are procedures commonly used to reduce the emission of volatiles during pitch processing and also to increase pitch carbon value, without altering most of the fundamental characteristics of the pitches (e.g., wetting capacity, fluidity, etc.). Basically, thermal treatment can be considered as an interrupted carbonization (350-450 °C) that involves distillation, polymerization and even the formation of mesophase. The result is pitches that are able to generate carbons with a lower porosity, higher density and pre-graphitic order. All these improvements make thermally treated pitches excellent precursors for matrices of different types of composites, carbon fibres, self-sintering graphites, etc. On the other hand, air-blowing has similar effects to thermal treatment but at lower temperatures (< 350 °C). This is because oxygen promotes the formation of free radicals that favour polymerization reactions. In this case, polymerization occurs via the formation of planar macromolecules and the formation of cross-linked structures. The latter prevents mesophase development during air-blowing. Table 1 summarizes the main characteristics of the treated pitches.

### TABLE 1. Main characteristics of treated pitches from coal-tar pitch (CTP) and anthracene oil-based pitch (AOP).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>C/H</th>
<th>SP</th>
<th>TI</th>
<th>NMPI</th>
<th>CY</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTP</td>
<td>none</td>
<td>1.80</td>
<td>1.64</td>
<td>97</td>
<td>20.0</td>
<td>4.7</td>
<td>34.6</td>
</tr>
<tr>
<td>TT-CTP</td>
<td>thermal treatment (430°C;3 h)</td>
<td>-</td>
<td>1.89</td>
<td>174</td>
<td>53.9</td>
<td>29.8</td>
<td>61.4</td>
</tr>
<tr>
<td>I-CTP</td>
<td>isotropic phase (filtration)</td>
<td>-</td>
<td>1.85</td>
<td>169</td>
<td>45.8</td>
<td>16.3</td>
<td>56.2</td>
</tr>
<tr>
<td>A-CTP</td>
<td>anisotropic phase (filtration)</td>
<td>-</td>
<td>2.05</td>
<td>&gt;300</td>
<td>66.7</td>
<td>53.4</td>
<td>74.9</td>
</tr>
<tr>
<td>AB-CTP</td>
<td>air-blowing (275°C; 30h)</td>
<td>1.86</td>
<td>1.87</td>
<td>210</td>
<td>52.0</td>
<td>27.1</td>
<td>62.7</td>
</tr>
<tr>
<td>AOP</td>
<td>none</td>
<td>-</td>
<td>112</td>
<td>3.0</td>
<td>2.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TT-AOP</td>
<td>thermal treatment (430 °C; 1.5 h)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-AOP</td>
<td>anisotropic phase (sedimentation)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* oxygen content (wt.%)
* carbon/hydrogen atomic ratio
* softening point (Mettler, °C)
* toluene-insoluble content (wt.%)
* N-methyl-2-pyrrolidinone-insoluble content (wt.%)
* carbon yield (900 °C, wt.%)
* mesophase content (vol.%)
The versatility for processing CTPs in order to enhance certain properties gives rise to materials with different structures and different properties. Thus, fluidity and a highly softening point are really desirable parameters for the preparation of carbon fibres. Fluidity permits the spinning of the fibre, while a high softening point prevents the spun pitch from deforming during stabilization and subsequent carbonization/graphitization. On the other hand, the affinity between the matrix precursor and the fibres (wetting capacity) and plasticity are the most relevant parameters for the preparation of C/C composites and self-sintering graphites, respectively. In this regard, air-blowing and thermal treatment are promising procedures for enhancing these properties.

From the arguments presented above it is clear that treated pitches have a great potential as precursors for obtaining carbon materials. Moreover, the coexistence of two phases in thermally treated pitches (isotropic fraction and mesophase) offer new possibilities for obtaining two additional precursors: the isotropic phase, mainly consisting of polymerized pitch, and the mesophase with an already established pre-graphitic order. Figure 2 illustrates in a succinct view of the possibilities for developing carbon materials from CTPs. In the following sections, synthetic graphites, carbon fibres and carbon fibre reinforced carbon composites will be described in a more detail.

![Figure 2. Traditional and advanced applications of coal-tar pitch.](image)

**Synthetic graphites**

Synthetic graphites are attractive materials for which applications are easily found in modern advanced technologies where a high chemical, mechanical, electrical and thermal performance is required (e.g., nuclear reactor walls, electrodes for electric discharge machines, etc.). Such useful combinations of properties are a consequence of the peculiar structure of these graphites, which consists of very fine anisotropic local units (microcrystallites) that confer an isotropic behaviour on the whole material. Carbonaceous mesophase is an excellent precursor for obtaining polygranular synthetic graphites, because mesophase is a self-sintering thermoplastic material, which is able to generate very pure, highly dense materials by thermal treatment in an inert atmosphere without the need for an external binder. This eliminates the tedious mixing and repetitive impregnation/carbonization steps involved in the traditional granular carbon technology used for preparing synthetic graphites.
The mechanism of mesophase growth in CTPs favours the formation of discrete microspheres. This is because at the initial stages of mesophase formation, QI particles tend to surround the mesophase making it more difficult to coalesce. The result is a mesophase, which is rich in microspheres and plastic enough to be moulded by pressing. Moreover, when the mesophase is excessively plastic, the mesophase plasticity can be gradually reduced by means of oxidative stabilization. After moulding and controlled carbonization/graphitization, CTP-based mesophase is able to produce graphites with a flexural strength of 80-100 MPa. Values above 100 MPa have been reached using anthracene oil–based mesophase as carbon precursor.

**Carbon fibres**

Carbon fibres show excellent structural, mechanical, electrical and thermal properties. For these reasons, they are widely used in structural and functional applications.

Pitch-based carbon fibres are usually grouped into two categories: (i) general purpose carbon fibres (GPCF) and (ii) high-performance carbon fibres (HPCF). Despite their different origins, both types of fibres are prepared following a similar sequence of steps: (i) spinning to generate the green fibre, (ii) stabilization to make the fibre infusible and (iii) carbonization to consolidate the structure of the carbon fibre. In the case of the HPCF, the processing also includes a graphitization step for achieving a higher graphitic order.

Coal-tar pitches have proved to be excellent precursors for both types of fibres. This is because CTPs have an aromatic composition that makes spinning and stabilization a process easily controllable. However, the use of CTPs in the preparation of fibres is obstructed by the problem of the solid particles (primary quinoline insolubles) which must be eliminated before processing in order to avoid the deformation of the fibre. For this reason, filtration or solvent extraction must be performed before processing. CTPs can be used to produce general purpose carbon fibres with a tensile strength of over 400 MPa and a modulus of almost 40 GPa. Anthracene oil-based pitches emerge as an alternative to CTPs in this application because of the total absence of solid particles that makes the tedious and time-consuming step of primary QI removal unnecessary.

**Carbon fibre reinforced carbon composites**

Carbon fibres are superb structural materials because of their excellent mechanical properties. However, their use in structural applications requires the presence of a second component (matrix), which confers stiffness and structural consistency on the material. The combination of fibres and matrix results in a composite in which the most positive characteristics of each individual component are linked. There are many types of composites. However, those made of carbon fibres and a carbonaceous matrix are especially interesting (carbon fibre reinforced carbon composites, C/C) because they preserve, and even improve, their mechanical properties with increasing temperature. This makes C/C ideal materials for use in extreme high-performance applications (e.g., aircraft brakes, components of aerospace shuttles, walls of nuclear reactors). The preparation of these composites involves the liquid impregnation of the fibres with pitch and the subsequent moulding/curing of the prepreg by pressing and carbonization up to ~ 1000 °C. The presence of QI in the composites exerts a great influence on both their mechanical strength and the mechanism of failure. CTPs with a high QI content (especially binder CTPs, ~ 10 wt.% of QI) give rise to matrices in which mosaics is the
predominant optical texture. These mosaics contribute to improving mechanical strength (400-500 MPa), but at the same time, give rise to a strong fibre/matrix adhesion that tends to fail via a catastrophic-like failure mechanism.

The properties of pitch based C/C composites can be improved substantially by densification. This procedure involves filling the open porosity of the composite by applying several cycles of impregnation/carbonization until the desired density and hence mechanical strength is achieved. An alternative to reducing the over long impregnation/carbonization cycles is to use high carbon yield pitches. As an example, the preparation of unidirectional composites from both thermally treated and air blown pitches offers the possibility of obtaining materials with a density and mechanical strength superior to those of untreated pitches, even when these have been previously densified (Table 2).

<table>
<thead>
<tr>
<th>Composite</th>
<th>Pitch treatment</th>
<th>db(^a)</th>
<th>P(^b)</th>
<th>ILSS(^c)</th>
<th>FS(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC-0</td>
<td>none (undensified)</td>
<td>1.50</td>
<td>16</td>
<td>15</td>
<td>416</td>
</tr>
<tr>
<td>CC-TT</td>
<td>thermal treatment</td>
<td>1.65</td>
<td>9</td>
<td>44</td>
<td>575</td>
</tr>
<tr>
<td>CC-AB</td>
<td>air-blowing</td>
<td>1.60</td>
<td>12</td>
<td>39</td>
<td>487</td>
</tr>
<tr>
<td>CC-5</td>
<td>none (3 densification cycles)</td>
<td>1.65</td>
<td>6</td>
<td>25</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\)bulk density (g cm\(^-3\))
\(^b\)porosity determined by optical microscopy (vol.\%)
\(^c\)interlaminar shear strength
\(^d\)flexural strength

CTP, and more specifically CTP-based mesophase, is also shown to be a superb infiltration agent for the impregnation/densification of carbon fibre performs. The high carbon yield, a highly suitable viscosity, low exudation capacity, and exceptional conductivity make CTP-based mesophase an ideal precursor for pitch infiltration in composites destined for frictional applications and other specialty utilities where high thermal conductivity is required (e.g., nuclear reactor walls).

Other carbon materials

Recent studies have proved the potential of CTP-based materials in other fields and for novel applications that are still being under research, such as anodic material for Li-ion batteries, graphite foams or graphitizable materials for supercapacitors.

Secondary Li-ion batteries are one of the most promising batteries because of their light weight, high working performance and environmentally-friendly composition. The anodic material of these batteries is composed of carbon. By using both isotropic pitch and mesophase it is possible to obtain carbons with a high capacity and good recycling behaviour.

Graphite foams are attractive materials that exhibit high thermal conductivity, very low density, high permeability and excellent thermal stability. Graphite foams can be obtained from a variety of precursors, one of which is CTP-based mesophase. The traditional preparation of these materials requires the use of thermal cycles under pressure in the presence of a blowing agent and a subsequent
pressure drop. The result is a material with a reticulated structure that has applications in several fields, such as that of heat exchangers, radiators or structural insulators.

Other types of material of great interest in carbon technology include those graphitizable materials that are able to generate porosity. CTP-based mesophase or CTP-based coke are unique precursors for obtaining activated carbons with a high electric conductivity. These materials are usually prepared by chemical activation (e.g. KOH), resulting in the formation of uniform micro and mesopores. Recent studies have shown that these carbons are superb materials for electrodes in supercapacitors. This is because CTP-based mesophase and CTP-based coke are able to generate high surface areas and can be easily prepared in the form required (e.g., powder, fibres, etc.). Moreover, graphitizable carbons offer many advantages over other materials, such as a better conductivity, a higher density or a higher yield during processing.

CONCLUDING REMARKS

Coal-tar pitches have been employed for more than a century in a large number of industrial processes. Although the main application of pitch is as a binder in aluminium and graphite technology, in recent years coal-tar pitches have been increasingly used as advanced carbon precursors because they are regarded as one of the most economical and abundant sources of carbon. Moreover, CTPs are very versatile and so it is possible to tailor carbons with a great variety of properties suitable for a wide range of applications. This makes coal-tar pitch an ideal candidate for competing in the emerging market of new materials. In conclusion, coal-tar pitch science can be considered as a dynamic field where technical and scientific aspirations strive to satisfy the growing needs of modern society. Moreover, the recent development in pitch production allows pitches from heavy tar distilled fractions (i.e., anthracene oil) to be obtained. These anthracene oil-based pitches represent a new generation of pitches with specific properties, and consequently, other potential applications which have still not been studied. Because of their origin, composition and behaviour, anthracene oil-based pitches can be considered as a hybrid from coal-tar pitch, petroleum pitch and synthetic pitch. Their low viscosity, high aromaticity and total absence of solid particles makes anthracene oil-based pitches a superb precursor for mesophase obtention, which implies in effect a new source of carbon materials.